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A Study of Hydrogen Adsorption in Pretreated Nanocarbon

Sang Moon Lee*, Satoshi Ohshima, Kunio Uchida and Motoo Yumura

*Japan Fine Ceramics Center, AIST Tsukuba Central 5, Tsukuba, Ibaraki 305-8565, Japan
Nanostructured Materials Team, Research Center for Advanced Carbon Materials, AIST Tsukuba Central 5, Tsukuba, Ibaraki 305-8565, Japan

ABSTRACT

A thermal treatment was applied with CO₂ and air for the development of a porous structure. Adsorption isotherms of nitrogen were measured on well-characterized Ni-C nanoparticles. The thermal treatment with CO₂ increased the total surface area and micropore volume. In addition, the thermal treatment with CO₂ increased the hydrogen adsorption.

INTRODUCTION

In recent years, the preparation of new materials, such as carbon nanotubes[1], carbon nanoparticles[2], and nanofibers[3] has been receiving much attention. These carbon nanomaterials are of interest from scientific and technological points of view, and they are expected to hold a great potential for application in various fields. In particular, the reversible storage of hydrogen on carbon nanotubes and nanofiber has been studied extensively[4-6]. Moreover, for adsorption utilization, opening of the potential adsorption space of nanotubes has been studied[7-8]. However, there has not been a study of gas adsorption on nanoparticles. Therefore, we investigated the pore structure, which plays an essential role in gas adsorption, as well as the properties of hydrogen adsorption and the surface properties of Ni-C nanoparticles. Ni-C nanoparticles with a diameter of 5-20nm were synthesized by the arc-discharge method. The particles were stable under the atmosphere because they were surrounded with a graphite sheet and amorphous carbon. Because Ni-C nanoparticles are nearly nonporous, the thermal treatment was applied with CO₂ and air in order to develop a porous structure. After that, the pore structure parameters of Ni-C nanoparticles before and after thermal treatment were investigated by high-resolution N₂ adsorption measurement at 77K. In addition, the surface properties of Ni-C nanoparticles were investigated by X-ray Photoelectron Spectroscopy (XPS). Hydrogen adsorption studies were performed using a gravimetric method in which weight changes in samples with gas adsorption were measured using a balance.

EXPERIMENTAL

Ni-C particles were synthesized by the arc-discharge method. Ni-C nanoparticles have a diameter of 5-20nm. Thermal treatment was respectively performed by CO₂ and air for development of a porous structure. Ni-C nanoparticles were heated in a CO₂ flow of 200mL/min at 1173K for 15min using a tubular furnace and in air atmosphere at 623K for 15min using a box furnace. Prior to the thermal treatment, TGA analysis of Ni-C nanoparticles was carried out to determine the temperature of thermal treatment in CO₂ and air, respectively. The micropore structures were determined by adsorption of N₂ at 77K using volumetric equipment (Quantachrome AS-1-MP) after preevacuation at 573K and 10⁻⁴ Pa for 24hr. IUPAC recommends the classification of pores according to pore width(*w*): micropores (*w*<2nm), mesopores (2<*w*<50nm), and macropores (*w*> 50nm). The micropore structural parameters were obtained from a high-resolution α_s -plot[9] using the standard adsorption data of highly crystalline nonporous carbon black (Mitsubishi 4040B). X-ray photoelectron spectroscopy (XPS) was used to determine the oxygen and nickel content on the surface of Ni-C nanoparticles. XPS spectra were measured using a PHI ESCA model 5800 (Physical Electronics Co.). The measurements were performed with Al K α under a vacuum pressure of <10⁻⁶ Pa at room temperature. The power of the monochromatized X-ray source was 100W.

Hydrogen adsorption studies were performed using a gravimetric method in which weight changes in samples with gas adsorption were measured using a balance. The high-pressure hydrogen adsorption isotherm was measured at 298K using a magnetic suspension balance (Mettler AT 261, resolution 0.01mg). High-purity hydrogen gas (99.99999%) was used after purification with a liquid nitrogen trap. The pretreatment prior to the adsorption measurement was performed under a vacuum (10⁻⁴ kPa) and a temperature of 573K for 2hr.

DISCUSSION

To predict the temperature of the thermal treatment, TGA analysis of Ni-C nanoparticles was carried out in air and CO₂. Figure 1 shows the TGA results of Ni-C nanoparticles. When air was used, the weight decreased sharply at around 818K. In a CO₂ atmosphere, however, the weight decreased at a much slower rate, and no significant reaction was observed below 1000K. Considering the TGA results in air and CO₂, thermal treatment was carried out at a temperature over 818K for air oxidation and 1173K for CO₂ oxidation.

The adsorption isotherms of N₂ at 77K for Ni-C nanoparticles, as-received and thermal-treated in air and CO₂, are given in Figure 2. Ni-C nanoparticles exhibit an isotherm of type II according to IUPAC classification without hysteresis. The Ni-C2 sample exhibits an isotherm

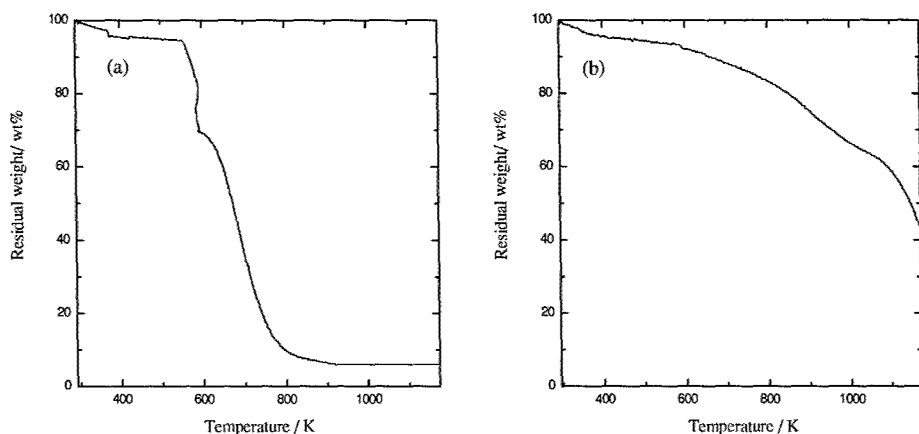


Figure 1. The TGA results of Ni-C nanoparticles: (a) in air, (b) in CO₂.

with a relatively high plateau. The high uptake in the adsorption isotherm at a relatively low pressure indicates the presence of micropores. The adsorption isotherms were analyzed with the subtracting pore effect (SPE) for a high-resolution α_s -plot. The α_s -plot on highly crystalline nonporous carbon black (Mitsubishi 4040B) was used as a standard isotherm. The pore structure parameters estimated by SPE are summarized in Table 1. The thermal treatment with air and CO₂ is accompanied with a substantial increase of the total surface area. In addition, the number of micropores increased significantly after the thermal treatment. Thus, the micropore volume of the Ni-C nanoparticle after oxidation in CO₂ at 1173K increased 2.7 times. The mesopore volume, V_{me} , estimated as the difference between the total pore (the volume filled at $P/P_0=0.98$) and micropore volume, is also given in Table 1. The mesopore volume increased after the thermal treatment. The mesopore volume ratio of Ni-C after the thermal treatment in air at 623K was much greater than that of Ni-C after thermal treatment in CO₂ at 1173K.

The surface chemical changes of Ni-C nanoparticles after the thermal treatment were examined by XPS. Figure 3 (a) shows that the XPS spectral change of the C1s peak coincides with that of graphitic carbon (284.6eV). All samples show a sharp graphitic carbon peak and a broad peak at 287-290eV. Figure 3 (b) shows the Ni2p XPS spectra of Ni-C nanoparticles. The as-received Ni-C nanoparticle (Ni-C0) has no Ni2p XPS peak, although the TGA result showed 6% of the residual amount. These results suggest that the Ni in the nanoparticle is coated with a graphene sheet. However, thermal-treated Ni-C nanoparticles (Ni-C1, Ni-C2) show typical Ni2p peaks of

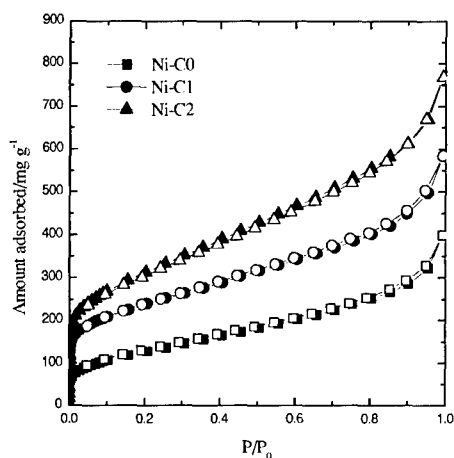


Figure 2. N_2 adsorption isotherms on as-received and thermal-treated Ni-C nanoparticles at 77K. Ni-C0: as-received sample; Ni-C1: thermal-treated Ni-C in air; Ni-C2: thermal-treated Ni-C in CO_2 . The solid and open symbols indicate adsorption and desorption, respectively.

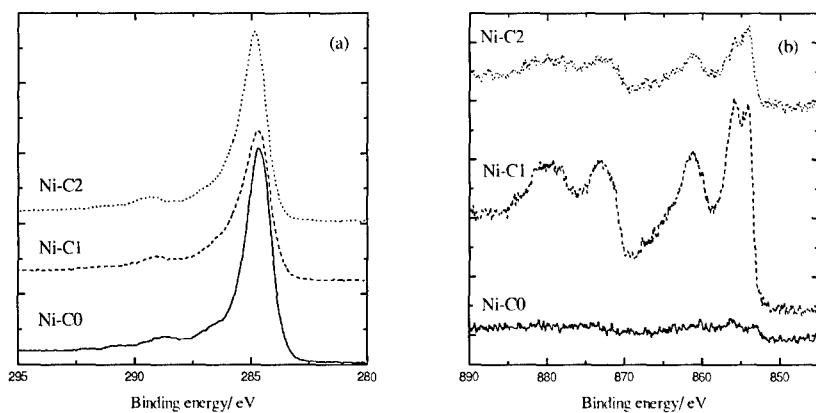


Figure 3. XPS spectra of as-received and thermal-treated Ni-C nanoparticles: (a) C1s, (b) Ni2p.

Table I. Pore structure of as-received Ni-C nanoparticles and thermal-treated Ni-C nanoparticles determined by the SPE method.

sample	pretreatment condition	S_t^a ($m^2 g^{-1}$)	S_{ext}^b ($m^2 g^{-1}$)	V_t^c ($mL g^{-1}$)	V_{mi}^d ($mL g^{-1}$)	V_{me} ($mL g^{-1}$)
Ni-C0	As-received	248	192	0.47	0.09	0.38
Ni-C1	air, 623K, 15min	548	342	0.68	0.15	0.53
Ni-C2	CO ₂ , 1173K, 15min	637	273	0.77	0.24	0.53

^a Total specific surface area, ^b External surface area, ^c Total pore volume, ^d Micropore volume.

NiO or Ni₂O₃ at 854.3 and 855.8 eV[10]. These results are due to the surface-etching effect by the thermal treatment with air and CO₂.

Figure 4 shows hydrogen adsorption isotherms at 298K on thermal-treated Ni-C nanoparticles. The adsorption equilibrium was achieved very quickly within 15min, and the adsorption was reversible. Consequently, hydrogen is adsorbed by physical adsorption. Thermal-treated Ni-C nanoparticles show an increase in the amount of hydrogen adsorption. The CO₂ treatment significantly improved the hydrogen adsorption because the micropores were developed more by the CO₂ than by the air treatment. Furthermore, an increase of the hydrogen adsorption was observed with increasing the specific surface area of Ni-C nanoparticles. Therefore, for increasing hydrogen adsorption, an enlargement of the specific surface area by the development of micropores was required.

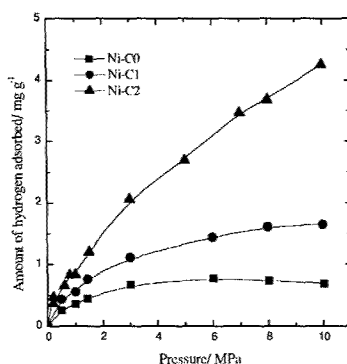


Figure 4. Hydrogen adsorption isotherms at 298K on thermal-treated Ni-C nanoparticles at 298K. Ni-C0: as-received samples; Ni-C1: thermal-treated Ni-C in air; Ni-C2: thermal-treated Ni-C in CO₂.

CONCLUSIONS

The hydrogen adsorption of as-received and thermal-treated Ni-C nanoparticles has been measured. The maximum hydrogen adsorption observed at 298K and 10M Pa is less than 5mg g⁻¹. Hydrogen is adsorbed by physical adsorption. Thermal-treated Ni-C nanoparticles show an increased hydrogen adsorption. The amount of adsorbed hydrogen in Ni-C nanoparticles can be described as a function-specific surface area and micropore volume.

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